Korean Chem. Eng. Res., 61(2), 322-327 (2023)
https://doi.org/10.9713/kcer.2023.61.2.322
PISSN 0304-128X, EISSN 2233-9558

Evaluation of Design of Experiments to Develop MOF-5 Adsorbent for Acetylene Capture

Min Hyung Lee*, Sangmin Lee and Kye Sang Yoo*,**†**

**Department of Energy & Chemical Engineering, Graduate School of Convergence Science, Seoul National University of Science and Technology, Seoul, 01811, Korea*
***Department of Chemical & Biomolecular Engineering, Seoul National University of Science and Technology, Seoul, 01811, Korea*
(Received 14 November 2022; Received in revised from 19 December 2022; Accepted 13 January 2023)

Abstract – A design of experiments was evaluated in optimizing MOF-5 synthesis for acetylene adsorption. At first, mixture design was used to optimize precursor concentration, terephthalic acid, zinc acetate dihydrate and N,N-dimethylformamide. More specifically, 13 conditions with various molar ratios were designed by extreme vertices design method. After preparing the samples, XRD, N_2 physisorption and SEM analysis were performed for their characterization. Moreover, acetylene adsorption experiments were carried out over the samples under identical conditions. The optimal precursor composition for MOF-5 synthesis was predicted on a molar basis as follows: terephthalic acid : acetate dihydrate : dimethylformamide = 0.1 : 0.4 : 0.5. Thereafter, multi-level factorial design was designated to investigate the effect of synthesis reaction conditions such as temperature, time and stirring speed. By the statistical analysis of 18 samples designed, 4 reaction parameters were determined for additional adsorption experiments. Therefore, MOF-5 prepared under the synthesis time and temperature of 100 ℃ and 12 h, respectively, showed the maximum adsorption capacity of 15.1 mmol/g.

Key words: MOF-5 synthesis, Acetylene adsorption, Design of experiments, Optimization

1. Introduction

Acetylene is an important raw material for the synthesis of various organic compounds such as 1,4-butanediol, which is widely used to produce polyurethanes and polyester plastics. However, one of the problems with acetylene is its shelf life. Acetylene is highly explosive compressed to more than 0.2 MPa at room temperature even in the absence of oxygen, making it difficult to store even in high-pressure steel cylinders. The current storage method is to dissolve the acetylene in acetone into a steel cylinder to prevent polymerization [1]. Thus, an advanced technique is crucial to solve the problem. Adsorption at low pressure using a porous material is considered as an alternative. So far, zeolites [2,3] and silica materials [4-6] are known to have desirable acetylene adsorption capacity.

Metal organic framework (MOF) is a new type of hybrid organic-inorganic microporous crystalline material that forms a three-dimensional structure connected by metal containing inorganic clusters and organic ligands. The metal clusters serve as the intersection of the three-dimensional structure, while the ligand generates a stable and regularly open structure. Thereafter, the molecular building blocks formed are assembled into a modularly designed composite to create various structures [7-11]. Recently, MOFs have received significant attention as porous materials with a higher surface area and various structures. In particular, the adsorption of MOFs, nonlinear optics, and catalytic applications have been conducted actively [12-18]. Among them, MOF-5 is one of the most intensively studied materials. It possesses a porous crystalline cubic structure by linking inorganic ZnO to benzene-1,4-dicarboxylate (BDC). The network intersections are constructed by Zn-containing clusters that act as octahedral secondary building units (SBUs), and the spacers are doubly substituted organic ligands. BDC molecules preserve the topology of the network and provide an accommodating way to regulate both pore size and framework function [8]. Optimization of the synthesis process of MOF-5 can be commercialized in many areas. However, as the synthesis steps are grown and the number of precursors increases, the experimental burden is boosted significantly. Therefore, the traditional trial and error method has main disadvantages in terms of time consumption and cost raising.

Design of Experiments (DOE) is a method of designing and analyzing experiments to infer valid and objective conclusions. DOE can describe as a series of tests in which the input factors intentionally change to determine the cause of a significant change in the response. This process includes planning, designing, and analyzing the experiment [19]. In particular, DOE is a reliable statistical method for developing a new process or analyzing an existing process for optimization. DOE generates valuable information using a specific experimental model while minimizing the number of actual

† To whom correspondence should be addressed.
E-mail: kyoo@seoultech.ac.kr

experiments. To date, DOE is widely applied in the manufacturing industry to improve product performance and reliability, process capability, and yield. Moreover, the application of DOE method to new research fields is gradually expanding [20-22]. In this study, various DOEs were used to synthesize MOF-5 as an adsorbent of acetylene adsorption. The analysis DOE method could help the development of an efficient adsorbent within a minimum number of experiments. Above all, we focused on verifying the effectiveness of DOE in the actual process.

2. Experimental

2-1. Preparation of MOF-5

Terephthalic acid (TPA, C_6H_4-1,4-$(CO_2H)_2$, 98%), zinc acetate dihydrate (ZnAc, $Zn(CH_3COO)_2 \cdot 2H_2O$, 98%), N,N-dimethylformamide (DMF, $HCON(CH_3)_2$, 99.8%) and ethanol (96%) were purchased from Sigma-Aldrich. All the chemicals were used without further purification. Initially, TPA was dissolved in a DMF and then ZnAc was added in the mixed solution. The amount of the precursors was adjusted to the designed concentration. The solution was then stirred at room temperature for 10 minutes to form a uniform solution. The stirring spread was controlled by homogenizer. Thereafter, the mixture was transferred to a Teflon-lined stainless-steel autoclave and kept at the designed temperature and time. The product mixture was then centrifuged to recover the solid product, which was washed with ethanol. The product was then dried at room temperature for 24 h.

2-2. Characterization of MOF-5

The powder XRD patterns of the catalysts were recorded using X-ray diffractometer (Shimadzu XRD-6000) operated at 40 kV and 30 mA using Cu Kα (λ = 0.15418 nm) radiation to determine the crystal structure. The surface area of sample was measured using N_2 sorption method with a BELSORP-MINI II instrument (BEL Co.). All samples were pre-treated with helium at 150 ℃ for 2 h before analysis. The sample images were confirmed using scanning electron microscopy (SEM, JEOL, JSM-6700F).

2-3. Acetylene adsorption

The adsorbent sample was activated in a helium atmosphere at 150 ℃ for 2 hours before acetylene adsorpton. An acetylene breakthrough test was performed using stainless steel tube at atmospheric pressure. For each run, 50 mg of adsorbent was loaded into the bed. Acetylene gas with a balanced nitrogen concentration of 1000 ppm (0.1%) passed through the fixed bed at a flowrate of 100 ml/min. Toluene was analyzed using gas chromatography (YL6500GC, Younglin Co., Ltd., Korea) equipped with flame ionization detector. The column installed BR-5 (Bruker, capillary 30 m × 0.25 mm), and the oven temperature was kept constant at 200 ℃. Breakthrough curves were used to investigate the performance of the adsorbents toward acetylene. The adsorption capacity (q) was as the total mass of the adsorbed acetylene per unit weight of MOF-5 (mg/g). It was calculated using the following equation:

$$q = \frac{QC_{in}}{m}\int_0^{t_s}\left(1-\frac{C_{out}}{C_{in}}\right)dt$$

where C_{in} and C_{out} are influent and effluent concentrations of acetylene (mg/m^3). Q is the volumetric flow rate (m^3/min), m is the total mass of MOF-5 (g) and t_s (min) is the time to reach saturation. The calculation was performed using MATLAB.

3. Results and Discussion

3-1. Effect of precursor ratio on MOF-5 properties

At first, mixture design method was used to decide optimal composition of precursors in MOF-5 synthesis. This method is a specific kind of response surface design to analyze the product with several components. Most of the results are expressed by the proportions of the individual ingredients in the mixture. For MOF-5 synthesis, three chemicals, TPA, ZnAc and DMF, were selected to optimize their composition. In this study, we used extreme vertex design, one of the mixture design methodologies that introduces additional constraints into the design because the lower and upper bounds of the component proportions are not 0 to 1. Indeed, the ranges used in the design were as follows; TPA + ZnAc + DMF = 1, 0.1 ≤ TPA ≤ 0.3, 0.3 ≤ ZnAc ≤ 0.6, 0.2 ≤ DMF ≤ 0.5. The values were based on molar concentration of the materials. In fact, a modified molar ratio was used to simplify the design of the mixture method. In particular, DMF was designed by reducing to 1/10. In the experiment, the actual moles of DMF was converted into 10 times from the amount used in design.

Thirteen compositions of the precursors based on mol ratio was designed by Minitab software. MOF-5 samples were synthesized with the predetermined precursor concentrations under identical reaction conditions, time, temperature and stir speeds. Then, characterizations were performed with XRD and N_2 physisorption methods. XRD analysis was performed to confirm the crystal structure of MOF-5 samples. Interestingly, the crystal structures of 13 samples could be divided into three phases. The XRD patterns of three most representative samples are presented in *Fig*. 1. The sample in which crystals were sufficiently grown to form a phase identical to MOF-5 structure was designated as phase 3. The phase with the least developed crystal structure was classified as phase 1. A structure with an XRD pattern intermediate between the two crystal structures was designated as phase 2. Thus, the composition ratio of the reactants was identified as an important factor to form the crystal structure.

Structural properties of the samples were determined by the nitrogen adsorption method. As a general trend, the MOF-5 sample with high crystallinity possessed a higher specific surface area (not shown). The adsorption isotherm of any adsorption system is referred to as a curve of the amount of adsorbed molecules to the adsorbent surface at constant temperature. Interestingly, the isotherm curves of the samples could be divided into three types as XRD pattern (see

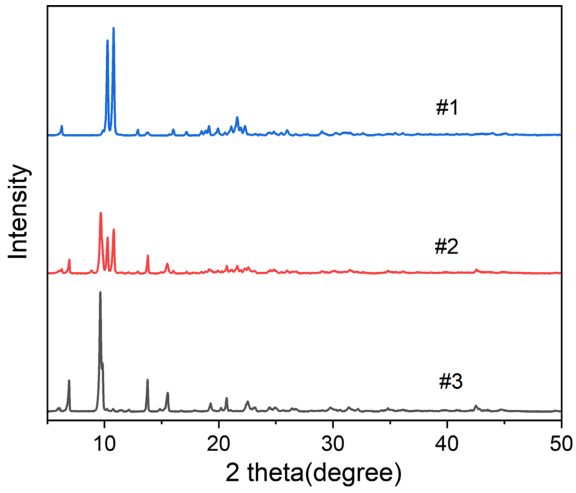

Fig. 1. XRD patterns of representative MOF-5 samples with different crystal development.

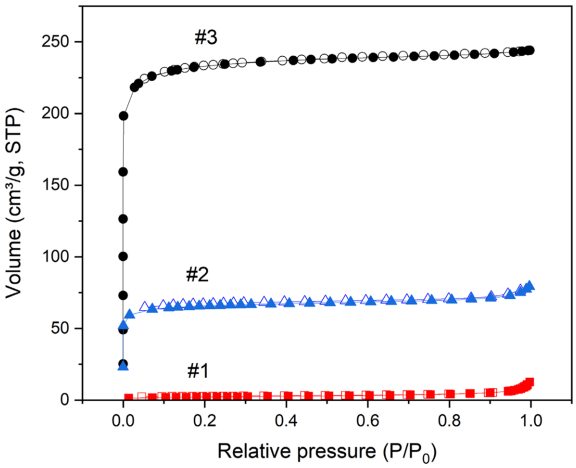

Fig. 2. Plot of adsorption and desorption isotherms of representative MOF-5 samples with different crystal development.

Fig. 1). With developing the crystal from amorphous, the isotherm became to type I according to the IUPAC classification. Type I adsorption isotherms describe the adsorption of gas molecules to the adsorbents having micropores such as MOFs and the surface of the adsorbent is covered with a monolayer of adsorbed molecules. SEM images of three selected MOF-5 samples are shown in *Fig*. 3. SEM micrographs of the phase #3 sample show high quality crystals with good shape, indicating that the particles are highly crystalline. This result is consistent with the results obtained from the XRD pattern (*Fig*. 1). However, the morphology of the phase 1 sample shows irregularity and a particle broadened distribution. Phase 2 sample shows an intermediate form that is similar to the results of the above characterizations.

3-2. Evaluation of MOF-5 properties by mixture design method

Acetylene adsorption experiments were performed on 13 adsorbents to measure adsorption capacity. Statistical analysis was then performed on the XRD phase and BET surface area along with their adsorption capacity. Fig. 4 shows the mixture contour plots for the XRD phase, BET surface, and adsorption capacity of the synthesized MOF-5 samples with various modified mol factions of precursors. Surprisingly, the analysis results for the three factors showed similar trends. This means the analysis of the XRD phase or BET surface area of adsorbents could predict the adsorption capacity of adsorbents using the design of the experimental method without actual adsorption experiments. Fig. 5 shows the cox response trace plot showing the effects of shifting each mixture component while holding all others in an identical ratio. The trace curves exhibit the effect of adjusting the corresponding component along an imaginary line (direction) linking the reference blend to a vertex. The plot could recognize the most important components and then plot them on a contour or surface plot. Indeed, the effect of all precursors on the adsorption capacity was detected in the plot. This was in good agreement with the results discussed in Fig. 4. The optimum molar ratio for MOF-5 synthesis was decided by the response optimizer tool that shows how different experimental settings affect the responses predicted. As shown in Fig. 6, MOF-5 synthesized under the modified mol ratio of 0.1:0.4:0.5 was predicted to show the maximum value for all conditions.

3-3. Evaluation of MOF-5 capability by multi-level factorial method

In general, the main factors in MOF synthesis are synthesis temperature, time, and stirring speed. In previous studies [23], those factors were shown to somewhat influence MOF synthesis. However,

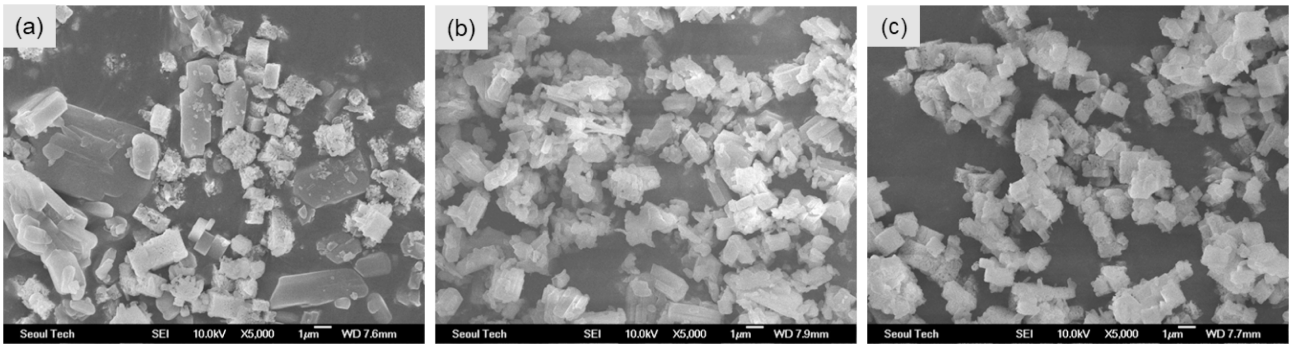

Fig. 3. SEM images of representative MOF-5 samples with different crystal development (a) phase #1, (b) phase #2, and (c) phase #3.

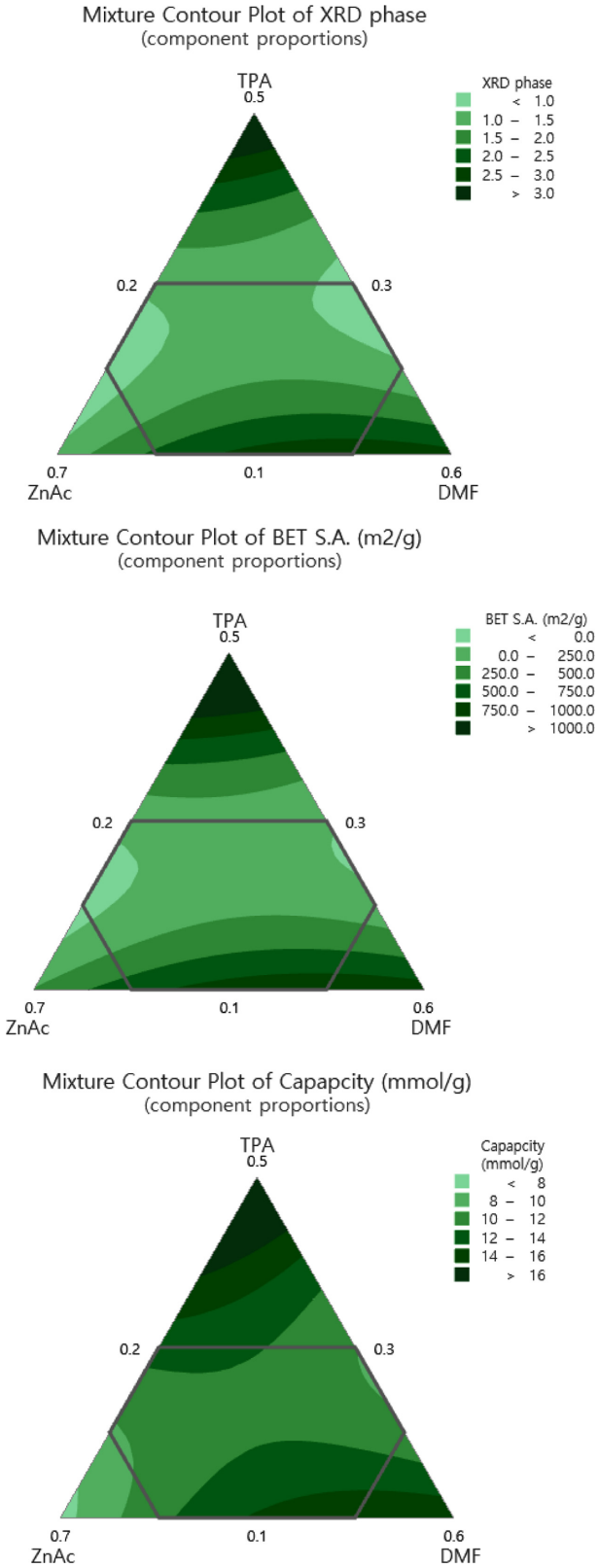

Fig. 4. Mixture contour plots of XRD phase, BET surface area and adsorption capacity of MOF-5 synthesized with various modified mol faction of precursors.

the effect of the stirring speed was insignificant compared to the others. Considering this fact, a multilevel factorial method was used to design the experimental conditions. As shown in Table 1, MOF-5

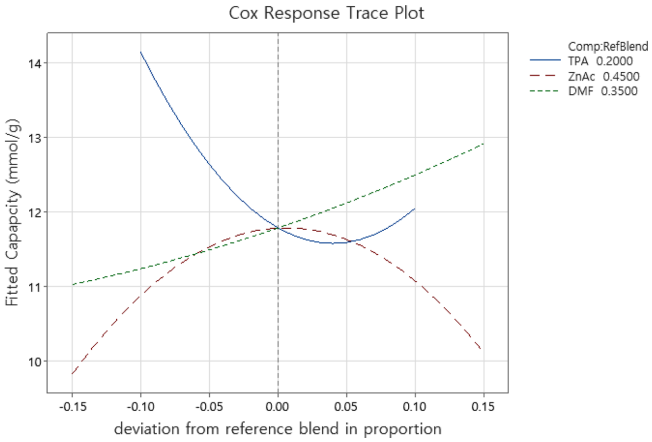

Fig. 5. Cox response trace plot of acetylene adsorption capacity of MOF-5 based on precursor composition.

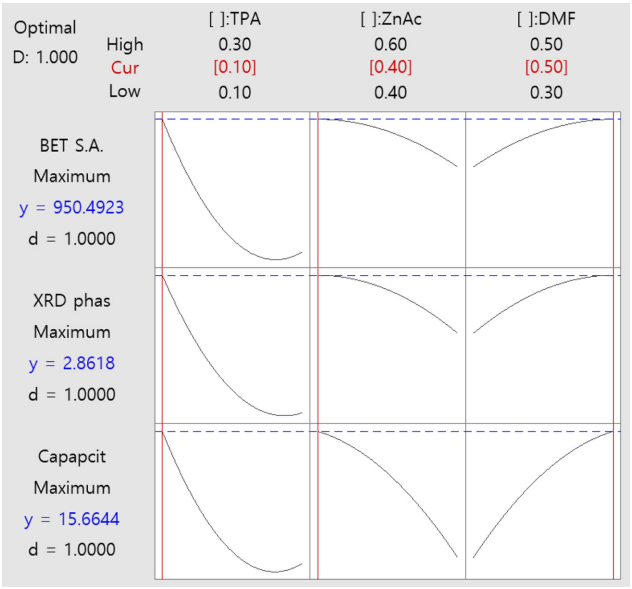

Fig. 6. Response optimization plot for the maximum values of MOF-5 synthesized with various modified mol fraction of precursors.

Table 1. Factor and level for multi-level factorial design

Factor	Level		
	low	Middle	High
Temperature (℃)	80	100	140
Time (h)	6	12	24
Speed (rpm)	0	-	800

synthesis conditions were selected in the three-step range of the synthesis temperature and time and the two-step range of stirring speed. As a result of the design, 18 conditions were determined and then synthesis experiments were performed accordingly. XRD phase and BET surface area of the samples were obtained by the characterizations. Based on these values, a response optimizer was used to predict the acetylene adsorption capacity. First, two factors, the BET surface area and the XRD phase, were set as variables, and then the conditions were predicted to obtain the maximum value.

Table 2. Summary of response optimizer results for XRD phase and BET surface area of MOF-5 samples

BET S.A.		XRD phase		Factors			Sample name
Max.	Min.	Max.	Min.	Temperature (℃)	Time (h)	Speed (rpm)	
√		√		100	12	0	Max-B
√				100	12	0	
		√		100	24	800	Max-X
			√	140	24	800	Min-X
	√			80	6	0	Min-B
	√		√	80	6	0	

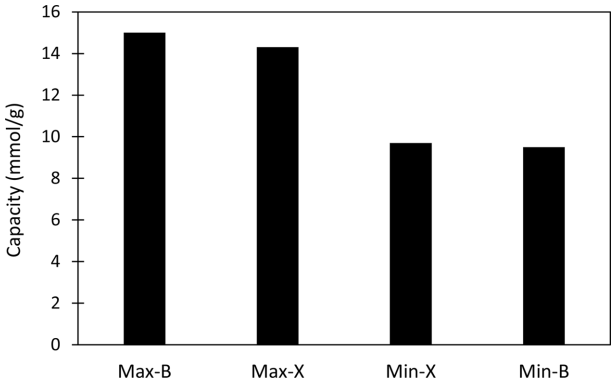

Fig. 7. Acetylene adsorption capacity of selected MOF-5 samples.

Conditions for obtaining the minimum value were also analyzed in the same way. As shown in Table 2, the same synthesis conditions were predicted when both values were used as variables at the same time and when only the BET surface area was used. These samples were named Max-B and Min-B, respectively. However, other synthesis conditions were predicted when optimization was performed using just the XRD phase value. MOF-5 samples synthesized under these two conditions were named Max-X and Min-X, respectively. An acetylene adsorption experiment was performed under identical conditions using four MOF-5 samples. As shown in Fig. 7, the adsorption performance of the Max-B sample was slightly better than that of Max-X. The adsorption capacity of the two samples, Min-B and Min-X, was almost comparable. Indeed, MOF-5 synthesized at 100 ℃ for 12 hours acquired maximum acetylene adsorption amount of 15.1 mmol/g.

4. Conclusions

Recently, a new type of research on the complex and sophisticated synthesis of nanoparticles has been attempted, and accordingly, the difficulty of optimizing the synthesis process is increasing. Statistical DOE is a novel approach to solve this problem. In this study, a statistical DOE was performed to analyze the MOF-5 synthesis for acetylene adsorption. The precursors used in the synthesis were optimized using a mixture design method. The optimal composition ratio was predicted using the response optimizer. This is desirable approach to determine the optimal composition with a minimum of experiments. Then, a multi-level factorial design method was used to optimize the synthesis reaction conditions. This is a method of selectively controlling the design range by considering the influence of reaction conditions. Consequently, it is more effective to replace the trial-and-error method used in traditional process optimization with the DOE method.

Acknowledgments

This study was supported by the Research Program funded by the SeoulTech (Seoul National University of Science and Technology).

References

1. Boese, R., Kirchner, M. T. W., Billups, E. and Norman, L. R., "Cocrystallization with Acetylene: Molecular Complexes with Acetone and Dimethyl Sulfoxide," *Angew. Chem. Int. Ed.*, **42**, 1961-1963(2003).
2. Breck, D. W., Eversole, W. G., Milton, R. M., Reed, T. B. and Thomas, T. L., "Crystalline Zeolites. I. The Properties of a New Synthetic Zeolite, Type A," *J. Am. Chem. Soc.*, **78**, 5963-5972 (1956).
3. Amaro, A. A. and Seff, K., "Crystal Structure of an Acetylene Sorption Complex of Zeolite 4A," *J. Phys. Chem.*,**77**, 906-910 (1973).
4. Reid, C. R. and Thomas, K. M., "Adsorption of Gases on a Carbon Molecular Sieve Used for Air Separation: Linear Adsorptives as Probes for Kinetic Selectivity," *Langmuir*, **15**, 3206-3218 (1999).
5. Newalkar, B. L., Choudary, N. V., Kumar, P., Komarneni, S. and Bhat, T. S. G., "Exploring the Potential of Mesoporous Silica, SBA-15, as an Adsorbent for Light Hydrocarbon Separation," *Chem. Mater.*, **14**, 304-309(2002).
6. Newalkar, B. L., Choudary, N. V., Turaga, U. T., Vijayalakshmi, R. P., Kumar, P., Komarneni, S. and Bhat, T. S. G., "Adsorption of Light Hydrocarbons on HMS Type Mesoporous Silica," *Micropor. Mesopor. Mater.*, **65**, 267-276(2003).
7. Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O'Keeffe, M. and Yaghi, O. M., "Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-organic Carboxylate Frameworks," *Acc. Chem. Res.*, **34**, 319-330(2001).
8. Eddaoudi, M., Kim, J., Rosi, N. L., Vodak, D., Wachter, J., O'Keeffe, M. and Yaghi, O. M., "Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage," *Science*, **295**, 469-472(2002).

9. Ockwig, N. W., Delgado-Friedrichs, O., O'Keeffe, M. and Yaghi, O. M., Reticular Chemistry: Occurrence and Taxonomy of Nets and Grammar for the Design of Frameworks," *Acc. Chem. Res.*, **38**, 176-182(2005).
10. O'Keeffe, M., Eddaoudi, M., Li, H., Reineke, T. M. and Yaghi, O. M., "Frameworks for Extended Solids: Geometrical Design Principles," *J. Solid State Chem.*, **152**, 3-20(2000).
11. Yaghi, M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M. and Kim, J., "Reticular Synthesis and the Design of New Materials," *Nature*, **423**, 705-714(2003).
12. Rosseinsky, M., "Recent Developments in Metal–organic Framework Chemistry: Design, Discovery, Permanent Porosity and Flexibility," *Microporous Mesoporous Mater.*, **73**, 15-30(2004).
13. Mori, W., Takamizawa, S., Kato, C. N., Ohmura, T. and Sato, T., "Molecular-level Design of Efficient Microporous Materials Containing Metal Carboxylates: Inclusion Complex Formation with Organic Polymer, Gas-occlusion Properties, and Catalytic Activities for Hydrogenation of Olefins," *Microporous Mesoporous Mater.*, **73**, 31-46(2004).
14. Sudik, A. C., Millward, A. R., Ockwig, N. W., Côté, A. P., Kim, J., Yaghi, O. M., Design, Synthesis, Structure, and Gas (N_2, Ar, CO_2, CH_4, and H_2) Sorption Properties of Porous Metal-Organic Tetrahedral and Heterocuboidal Polyhedra," *J. Am. Chem. Soc.*, **127**, 7110-7118(2005).
15. Snurr, R., Hupp, J. and Nguyen, S. B., "Prospects for Nanoporous Metal-organic Materials in Advanced Separations Processes," *AIChE J.*, **50**, 1090-1095(2004).
16. Rowsell, J. L. C. and Yaghi, O. M., "Strategies for Hydrogen Storage in Metal-organic Frameworks," *Angew. Chem. Int. Ed.*, **44**, 4670-4679(2005).
17. Millward, A. R. and Yaghi, O. M., "Metal−Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature," *J. Am. Chem. Soc.*, **127**, 17998-17999 (2005).
18. Bordiga, S., Lamberti, C., Ricchiardi, G., Regli, L., Bonino, F., Damin, A., Lillerud, K. P., Bjorgen, M. and Zecchina, A., "Electronic and Vibrational Properties of a MOF-5 Metal–organic Framework: ZnO Quantum Dot Behaviour," *Chem. Commun.*, 2300-2301(2004).
19. Bisgaard, S., "Industrial Use of Statistically Designed Experiments: Case Study References and Some Historical Anecdotes," *Quality Eng.*, **4**, 547-562(1992).
20. Sedghamiz, M. A., Raeissi, S, Attar, F., Salimi, M. and Mehrabi, K., "In-situ Transesterification of Residual Vegetable oil in Spent Bleaching Clay with Alkali Catalysts Using CCD-RSM Design of Experiment," *Fuel*, **237**, 515-521(2019).
21. Seki, Y., Seyhan, S. and Yurdakoc, M., "Removal of Boron from Aqueous Solution by Adsorption on Al_2O_3 Based Materials Using Full Factorial Design," *J. Hazard. Mater.*, **138**, 60-66(2006).
22. Ilzarbe, L., Alvarez, M. J., Viles, E. and Tanco, M., "Practical Applications of Design of Experiments in the Field of Engineering: A Bibliographical Review," *Qual. Reliab. Engng. Int.*, **24**, 417-428(2008).
23. Lee, M. H. and Yoo, K. S., "Optimization of MOF-801 Synthesis Using Sequential Design of Experiments," *Appl. Chem. Eng.*, **32**, 621-626(2021).

Authors

Min Hyung Lee: Graduate Student, Department of Energy & Chemical Engineering, Graduate School of Convergence Science, Seoul National University of Science and Technology, Seoul, 01811, Korea; mhlee11@seoultech.ac.kr

Sangmin Lee: Graduate Student, Department of Chemical & Biomolecular Engineering, Seoul National University of Science & Technology, Seoul 01811, Korea; leesangmin0529@dsmetal.com

Kye Sang Yoo: Professor, Department of Chemical & Biomolecular Engineering, Seoul National University of Science & Technology, Seoul 01811, Korea; kyoo@seoultech.ac.kr